



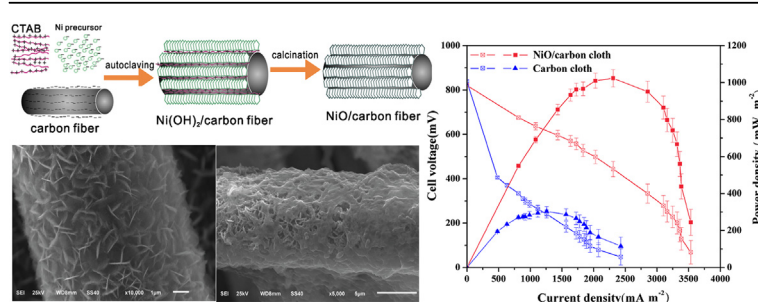
Short communication

Interfacial electron transfer of *Shewanella putrefaciens* enhanced by nanoflaky nickel oxide array in microbial fuel cellsYan Qiao^{a,b,c,1}, Xiao-Shuai Wu^{a,b,c,1}, Chang Ming Li^{a,b,c,*}^a Chongqing Key Laboratory for Advanced Materials & Technologies of Clean Energies, Southwest University, Chongqing 400715, China^b Institute for Clean Energy & Advanced Materials, Southwest University, Chongqing 400715, China^c Faculty of Materials & Energy, Southwest University, Chongqing 400715, China

HIGHLIGHTS

- A NiO nanoflaky array on the surface of carbon cloth fibers has been developed.
- The NiO nanoflaky array improves the interfacial electron transfer of MFC anode.
- The NiO/carbon cloth anode achieves 3-fold higher power density over carbon cloth.
- NiO/carbon cloth anode is very promising for high performance, large scale MFCs.

GRAPHICAL ABSTRACT



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ABSTRACT

A uniform nanoflaky nickel oxide (NiO) array is constructed on carbon cloth via optimized conditions, and further employed as an anode in *Shewanella putrefaciens* (*S. putrefaciens*) microbial fuel cells (MFCs). Results indicate that the NiO nanoflakes/carbon cloth anode significantly improves the MFC performance in comparison to the unmodified carbon cloth, delivering about three times higher power density. This attributes to an enhanced interfacial electron transfer rate between bacteria cell and nanoflaky NiO array-modified carbon fiber and improved adhesion of bacteria cells on the modified carbon fiber for more active reaction centers. Considering the facile synthesis process, low cost and long discharging lifetime, this NiO/carbon cloth anode could be very promising to be applied for high performance, large scale MFCs.

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1. Introduction

Microbial fuel cell (MFC) as a renewable energy source has received great attention in recent years [1–3]. MFCs are capable of

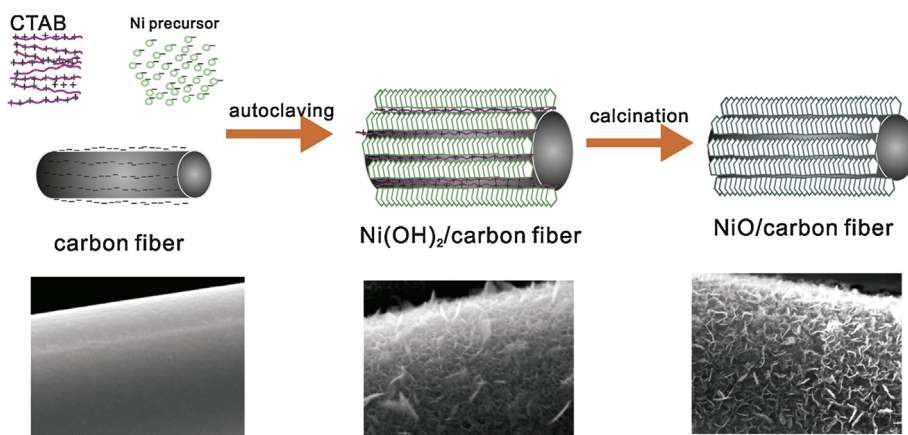
converting the potential energy reserved in wastewater or organic wastes directly into electricity while cleaning environment [2,4–6]. However, the sluggish electron transfer between electrode and bacteria and poor long-term stability result in a poor energy conversion efficiency and relatively low power density, thus severely limiting practical applications of MFCs [7,8].

To increase the power density, fabrication of electrode materials in nanoscales for high electrocatalytic performance and bioengineering microbe strains for improved biocatalytic ability have been investigated [7,9,10]. Among them, a facile approach is often to

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Scheme 1. Fabrication process of NiO nanoflaky on carbon fiber.

modify conventional anode materials for enhancement of electro-catalytic performance towards fuel oxidation. Logan et al. have demonstrated that treated carbon cloth with ammonium could increase the adhesion of bacteria during reactor start up, and enhance the efficiency of electron transfer from the bacteria to the electrode surface [11]. In another work, an oxidized graphite carbon cloth could achieve higher current density than untreated carbon cloth [12]. To achieve high density of layered biofilm, Chen et al. have developed a highly porous carbon fiber mat through layer-by-layer electrospinning of polyacrylonitrile onto a thin natural cellulose paper followed by carbonization [13]. Recently, some works about nanomaterials modified conventional carbon electrode achieving higher power density have been reported [14–17]. In these reports, the nanomaterials are just coated on the surface of carbon cloth or carbon paper. It is hard to obtain uniform nanostructure on carbon fiber surface and the poor contact between the coating materials and carbon fibers will affect the charge transfer at the bacteria–electrode interface. To solve this problem, it is necessary to fabricate carbon cloth fiber with *in situ* grown nanostructured materials.

Nickel oxide (NiO) is a low cost, environment friendly material and has been investigated as an electrode material in batteries and supercapacitors due to its high theoretical capacitances [18].

According to recent reports, increasing the capacitance of anode could eliminate the power overshoot phenomenon of MFCs and enhance the power output performance [19,20]. Introducing a high capacitance electrode material into carbon cloth will improve the performance of MFC anode. On the other hand, NiO has several oxidation statuses for fast reversible redox reactions [21]. In this case, the NiO can be used as electron mediators to accelerate the electron transfer between the bacterial cells and the carbon cloth electrode. So far, various nanostructures of NiO have been reported such as nanoplates, nanosheets or nanoribbons, nanowires, nanotubes, and hollow nanospheres [22]. Different synthetic methods like wet chemistry, hydrothermal preparation and electrodeposition are used for the nano NiO production [23]. Among these methods, it is easier to obtain well-crystalline materials with uniform nanostructures from hydrothermal preparation. Meanwhile, the hydrothermal synthesis technology has been used in chemical industry so that it provides a possibility for mass production of the electrode materials.

In this work, NiO nanoflaky arrays grown on carbon cloth fiber were fabricated via hydrothermal reaction. A cationic surfactant – hexadecyl trimethyl ammonium bromide (CTAB) was used to control the morphology of the composite materials and prevent the NiO nanoflakes to aggregate to be flowers or spheres. The ratio of CTAB and NiO were optimized as well as the reaction time and

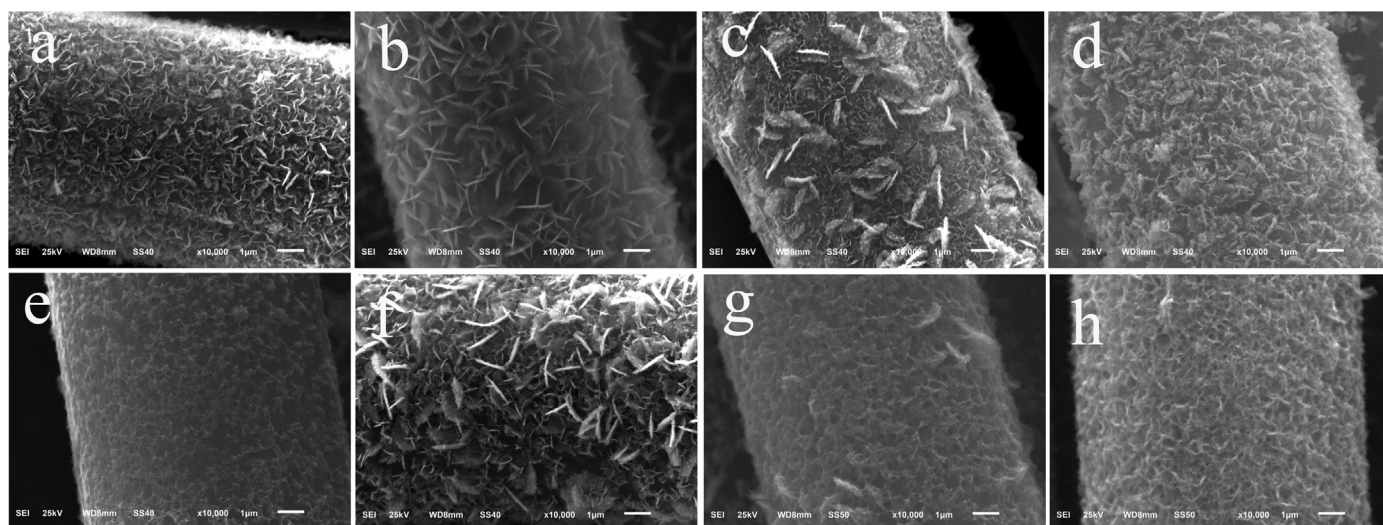


Fig. 1. SEM images of NiO/carbon cloth electrodes prepared at different processing methods (a: 150 °C–6h–1:1, b: 150 °C–6h–1:2, c: 150 °C–6h–1:4, d: 150 °C–6h–1:8, e: 120 °C–6h–1:2, f: 180 °C–6h–1:2, g: 150 °C–3h–1:2, h: 150 °C–9h–1:2).

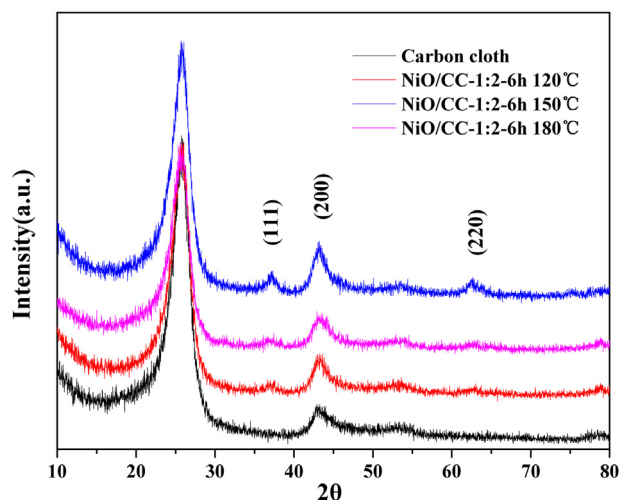


Fig. 2. XRD of NiO/carbon cloth electrodes prepared at different temperature process.

temperature. The bioelectrocatalytic behaviors of different NiO/carbon cloth anodes in *S. putrefaciens* MFC were investigated and the mechanism for the enhanced performance by NiO nanoflakes was discussed. To the best of our knowledge, this structure of nanoflakey NiO/carbon cloth composite is for the first time fabricated and applied in MFCs.

2. Materials and methods

2.1. Synthesis of NiO arrays on carbon cloth

All carbon cloth substrates were cleaned in 0.1 mol L⁻¹ H₂SO₄ solution prior to deposition. In a typical hydrothermal growth, 0.03 mol L⁻¹ nickel chloride was prepared with 50 mL of deionized water under vigorous stirring. 0.045 mol L⁻¹ CO(NH₂)₂ was then added to the solution. In order to control the morphology, CTAB was added in the solution, the molar ratio of CTAB and Ni²⁺ was 1:1, 1:2, 1:4 and 1:8 (the concentration of Ni²⁺ is constant in all samples). After all of the chemicals were fully dissolved, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave. A piece of carbon cloth was subsequently soaked in the solution, followed by heating the autoclave to 120 °C, 150 °C or 180 °C and it was kept there for 3, 6 or 9 h (Scheme 1). The as-synthesized electrodes prepared by the hydrothermal was then taken out, washed several times with deionized water and ethanol, dried at 80 °C for about an hour, and calcinated at 350 °C for 2 h.

2.2. Characterization

Scanning electron microscopy (SEM, JSM-6510LV, Japan) was used to investigate the morphology of as-prepared electrode materials. X-Ray diffraction (XRD) measurements were performed on a Shimadzu diffractometer (XRD-7000, Tokyo, Japan) operated in the reflection mode with Cu Kα radiation at a step size of 0.06° per

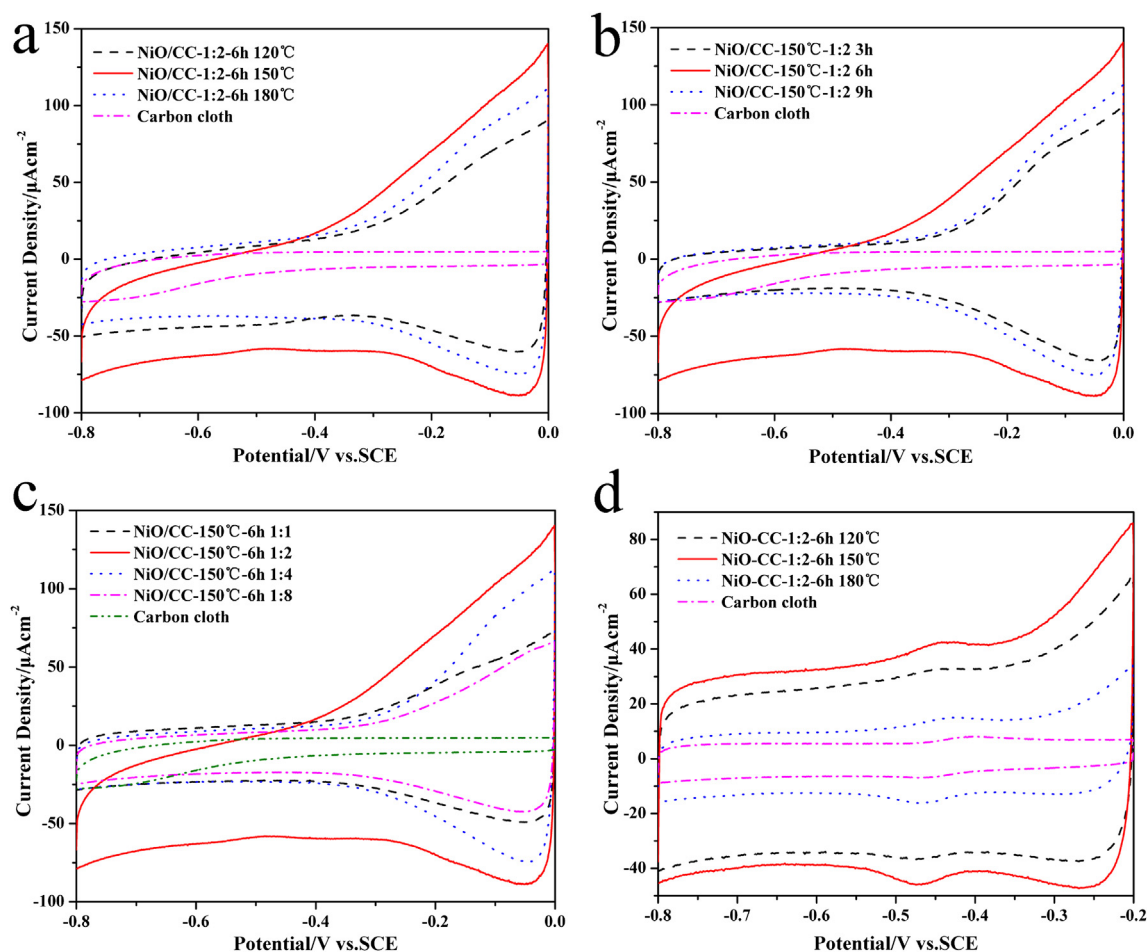


Fig. 3. Cyclic voltammograms of NiO/carbon cloth electrode at different processing methods (a: 1:2–6h with different temperature, b: 150 °C-1:2 with different time c: 150 °C-6h with different molar ratio of CTAB and Ni) conducted in 0.1 M PBS. d: Cyclic voltammograms of bacteria adhered electrodes conducted in PBS.

second. Before morphology observation, the discharged bacteria-absorbed anodes were immersed in 4% polyoxymethylene for 12 h and then sequentially dehydrated with ethanol (30%, 40%, 50%, 60%, 70%, 80%, 90%, 100%) and dried in vacuum at room temperature overnight.

Classic H-shaped MFCs were constructed with two 120 mL glass flasks. A Nafion 117 membrane was clamped in a 3.5-cm-diameter tubular (8 cm in length) junction (Fig. S1) to separate the anodic chamber and cathodic chamber. The anode and cathode were placed in the tubular junction close to the membrane to get a shortest distance. The projecting area of anode was 2 cm² and the anolyte was lysogeny broth (LB) medium contained: 10 g L⁻¹ sodium chloride, 10 g L⁻¹ tryptone, 5 g L⁻¹ yeast extract, pH = 7. A Fe(III)-reducing bacterium strain, *S. putrefaciens* that has been reported to possess direct electrochemistry ability [24,25] was used. In this work, the bacterium was cultured under shaking at 30 °C for 10 h to a concentration of $\sim 10^8$ cfu ml⁻¹ in a flask containing 100 mL standard LB medium and was further harvested by centrifuging at 4 °C (6000 rpm, 5 min). The culture was then transferred to the anodic chamber and nitrogen was purged for 30 min to remove oxygen before every test. The polarization and power output curves were measured by varying the output load resistor from 0.2 kΩ to 8 kΩ to monitor the steady-state current, which is measured until a stable reading can be obtained after changing the output load. The cathodic electrolyte was 50 mM potassium ferricyanide in 0.1 M phosphate buffered saline (PBS) (pH 7.4).

2.3. Electrochemical measurements

The electrochemical measurements were conducted in an anode limited half-cell with an SCE as the reference electrode and a titanium plate counter electrode. For the measurement in phosphate buffer saline (PBS, 0.1 M, pH 7), the biofilm adhered NiO/carbon cloth electrode was rinsed with DI water and washed in a stirring PBS solution to remove the adsorbed medium and metabolites. Cyclic voltammograms (CVs) and electrochemical impedance spectroscopy (EIS) experiments were performed by using a potentiostat (CHI660E, Shanghai Chenhua, China). The electrochemical impedance was measured on NiO/carbon cloth electrodes over a frequency range of 0.01 Hz–100 KHz at -0.45 V with a perturbation signal of 10 mV. Except otherwise stated, the voltammograms were recorded with a scan rate of 30 mV s⁻¹. All tests were conducted at room temperature.

3. Results and discussion

The SEM (scanning electron micrograph) images of NiO/carbon cloth fiber composites prepared with different conditions are shown in Fig. 1 and Fig. S2. It can be found that the NiO flakes vertically grow on the surface of carbon fiber to form a uniform array especially at high CTAB to Ni ratio (Fig. 1a and b). As the increasing ratio of Ni, the flakes become thicker, denser and non-uniform (Fig. 1c). When the CTAB to Ni ratio decreases to 1:8 and lower, the NiO film begins to exfoliated from the fiber and the NiO flakes accumulated to become spheres or flowers (Fig. S2i). It indicates that the CTAB play a key role in the growth of NiO flakes on carbon fiber surface. Besides the precursor ratio, the temperature and the reaction time also affect the morphology of the NiO nanoflakes. When the temperature increases from 150 °C to 180 °C, the flakes become thicker and denser (Fig. 1f), which is similar with the product prepared at 150 °C with 1:4 CTAB to Ni ratio. The reason might be that at higher temperature or higher concentration of Ni²⁺, the reaction rate of Ni(OH)₂ formation is too fast to form uniform structures. When the temperature is down to 120 °C, there

are only particles rather than flakes can be found on the fiber surface that could be due to the slower reaction rate. For the reaction time variation, the products obtained after 3 h or 9 h do not show the vertical-flake like morphology of NiO. The high magnification SEM micrographs (Fig. S2a–f) also display the same profiles. The vertical NiO nanoflakes structure can only obtained with the condition of 150 °C (hydrothermal reaction temperature), 6 h reaction time and 1:2 ratio of CTAB to Ni (denoted as 150 °C-6 h-1:2). The NiO nanoflakes connect with each other to form a network while greatly increasing the surface roughness of the carbon fiber. The above results suggest that the NiO/carbon fiber composite obtained at the condition of 150 °C-6 h-1:2 could deliver better electrocatalytic performance over other products due to the uniform growth of vertical NiO nanoflakes. As the morphology of composites prepared at different temperatures shows much more differences, these three NiO/carbon cloth composites are used as representatives for following analysis.

X-ray diffraction measurements were employed to investigate the crystal phase and structure of the synthesized composites. As shown in Fig. 2, the diffraction peaks corresponding to pure NiO appearing at $2\theta = 37.2^\circ, 43.2^\circ, 62.8^\circ$ can be readily indexed as (111),

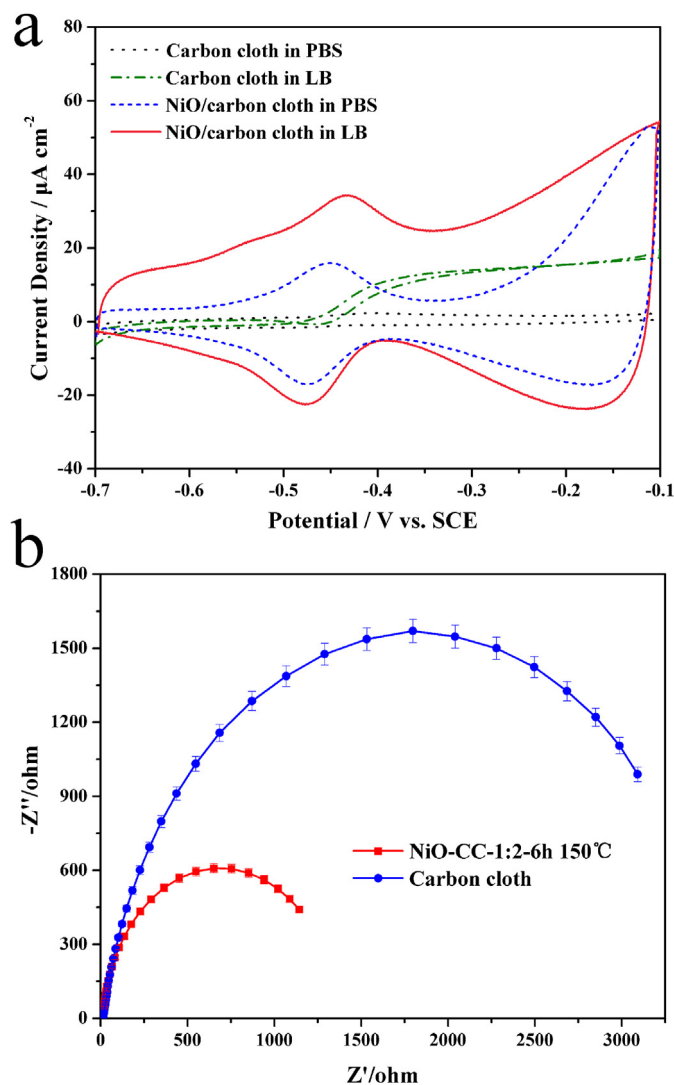


Fig. 4. a: Cyclic voltammograms (background subtracted) of bacteria adhered carbon cloth and NiO/carbon cloth anode measured in PBS and LB medium. b: Nyquist plots of carbon cloth and NiO/carbon cloth anode measured in LB medium.

(200) and (220) crystal planes [26]. The presence or absence of these peaks will indicate the structure of NiO crystals. As shown in Fig. 2, all of the characteristic diffraction peaks only can be found on the XRD pattern of NiO/carbon cloth prepared at 150 °C. No obvious shifting of peaks or other impurity phase can be detected. It suggests that the vertical NiO nanoflakes possess good crystal structure.

The specific surface area of NiO/carbon cloth electrode was examined using an automated gas sorption system (NOVA4000e, Quantachrome Instruments). The surface area increased by 62.3% after NiO deposition on carbon cloth (Fig. S3). While for different NiO/carbon cloth composites prepared by different conditions, no big difference of the specific surface areas is observed. Since the capacitive current is proportional to the active surface area of NiO, it could be used to evaluate the electroactive surface area of the electrode. Thus, their electrochemical capacitive behaviors were investigated in phosphate buffer (pH 7, 0.1 M). The data (Fig. 3a–c) show that after modification with nano NiO, the capacitive current of the carbon cloth electrode is significantly increased. It is noted that the composite electrode prepared at 150 °C-6 h-1:2 condition has the largest capacitive current and the changing profile of the capacitive current has a good agreement with the morphology changing. This suggests that the uniform vertical NiO nanoflakes array possess highest electroactive surface area. To further investigate the electrochemical behavior of the NiO/carbon cloth electrodes, the CV curves were measured in the phosphate buffer after bacteria cell adhered on electrode (Fig. 3d). A well-defined redox pair displays in the CV curve for each composite electrodes. Since no electron mediator is added in the PBS this pair of redox peaks could be ascribed to the direct electrochemistry behavior of the *S. putrefaciens*/NiO/carbon cloth anode. It is noted that the composite electrode prepared at 150 °C-6 h-1:2 condition possesses the

smallest peak separation and highest peak current (Table S1), indicating that the NiO nanoflakes grown on the carbon fiber can greatly improve the interfacial charge transfer. This optimized NiO/carbon cloth electrode will be used in following analyses.

To examine the electrocatalytic performance of the composite electrode, cyclic voltammograms and electrochemical impedance spectra of the bacteria adhered NiO/carbon cloth electrode and carbon cloth electrode were measured in different electrolyte (Fig. 4a). To exclude the influence of capacitive current, the background is subtracted for each CV curve. The results show that an obvious anodic catalytic current can be found on both carbon cloth and NiO carbon cloth. The oxidation peak potential for NiO/carbon cloth is more negative (−0.43) than that of carbon cloth (−0.38) and the peak current of NiO/carbon cloth ($19.5 \mu\text{A cm}^{-2}$) is about two times higher than that of carbon cloth ($10.2 \mu\text{A cm}^{-2}$), indicating significant improvement of the electrocatalytic performance.

The Nyquist plots were measured for three times and average values with standard deviation were plotted in Fig. 4d. A reported popular equivalent circuit model [27,28] (Fig. S4) was used to fit the results, indicating that the charge transfer resistance of NiO/carbon cloth anode is much smaller than that of carbon cloth. The charge transfer resistance (R_{ct}) of carbon cloth is more than two times higher than that of NiO/carbon cloth anode, which revealing that the NiO/carbon cloth anode possesses much faster interfacial charge transfer than carbon cloth anode. This result is in complete agreement with the CV data. The reason might be the denser NiO nanoflake array adhere on carbon cloth promotes the direct electrochemistry between the bacterial cells and the electrode. The vertical NiO nanoflakes may provide a better physical contact to the bacteria cell surface so that the outer membrane cytochromes could transfer the electrons to the electrode via the nanoflakes.

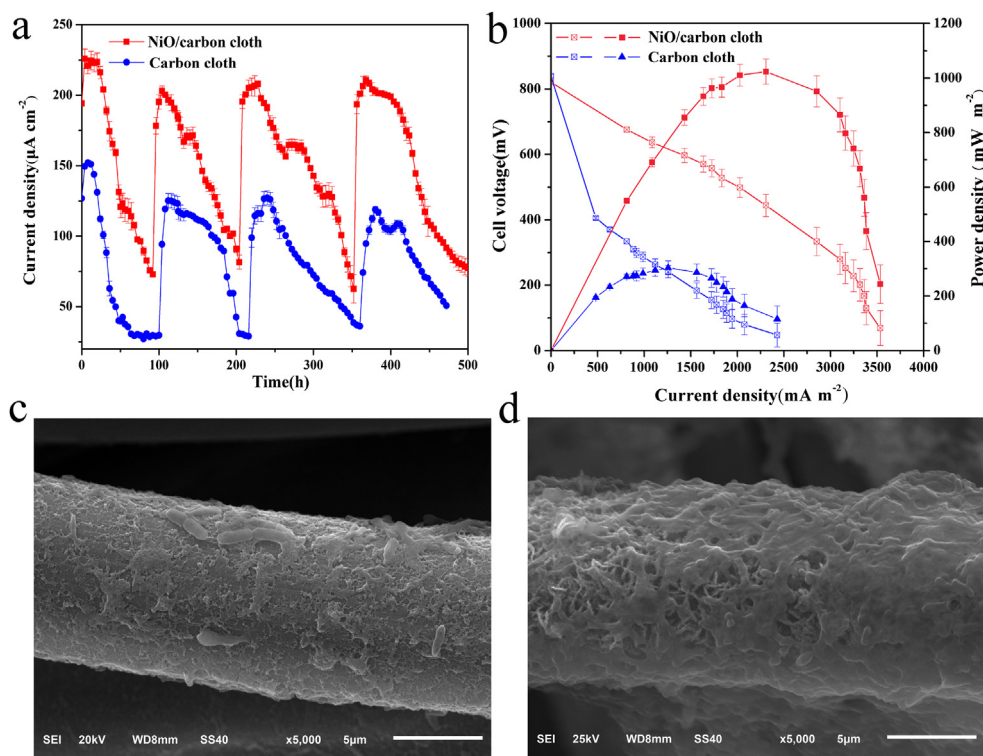


Fig. 5. Discharge performance — a, power curves and polarization curves — b of MFCs with different anodes. SEM micrographs of *S. putrefaciens* cells adhered on carbon cloth — c and the NiO-carbon cloth — d electrode surface.

The performances of both NiO/carbon cloth and plain carbon cloth anode-based MFCs were examined in a batch feed mode for four cycles. When the current dropped to 20% of the maximum value, the medium in the anode chamber was refreshed. The discharging curves (Fig. 5a) show that NiO/carbon cloth anode has achieved a significant higher power current density than carbon cloth anode. As the anolyte in both MFCs are same, the MFC with NiO/carbon cloth anode possesses much higher Coulombic efficiency than the one with carbon cloth anode. It is also noted that the current density NiO/carbon cloth MFC reaches almost same plateau in each cycle. This indicates that the NiO/carbon cloth anode is stable for long time operation. The output power density curves and polarization curves with average values and standard deviations in Fig. 5b show that the NiO/carbon cloth anode delivers a maximum power density of $1024 \pm 46 \text{ mW m}^{-2}$, which is more than 3-fold higher than that of the plain carbon cloth anode ($303 \pm 25 \text{ mW m}^{-2}$). After discharge, the surface morphology of the NiO/carbon cloth and the plain carbon cloth anode were examined by SEM. The images (Fig. 5c and d) show that on the unmodified carbon fiber only several bacterial cells can be observed. While on the NiO nanoflakes modified carbon fiber, the cell density is quite high and cells adhere with each other to form a biofilm. The biofilm firmly covers almost the entire surface of the composite fiber to load much larger amount of biocatalysts on NiO/carbon cloth anode than that on plain carbon cloth, resulting in the higher electrocatalytic current.

Considering that the surface hydrophilicity could affect the bacteria adhesion, the water contact angle of carbon cloth and NiO/carbon cloth were measured. The results (Fig. S5) suggest that the untreated carbon cloth has a quite hydrophobic surface. However, after modification with NiO nanoflakes, the surface becomes highly hydrophilic one. To explain this phenomenon, the FTIR spectra (Fig. S6) of both electrodes were measured. Since only some characteristic peaks of NiO can be found in the spectra, the increased hydrophilicity should be attributed to the modification of NiO nanoflakes. These results indicate that the NiO/carbon cloth electrode provides an excellent host for *S. putrefaciens* cells growth and boosts the interfacial direct electron transfer by offering better physical contact sites for the cells.

4. Conclusions

In summary, this work, the NiO nanoflakes array structure has been successfully grown on carbon fiber surface as a composite anode for MFCs. The composite anode significantly improves the MFC performance compared with the unmodified carbon cloth anode. The NiO/carbon cloth anode delivers an around 3-fold higher maximum power density higher than that of the plain carbon cloth anode due to the unique nanostructure for high electrocatalytic activity contributed from improved active surface area of electrode, strengthened adhesion of bacteria and enhanced interfacial charge transfer between bacteria cells and electrode. Furthermore, the electrode material NiO/carbon cloth is quite stable in an MFC system for long-term discharging. Considering the

synthesis process is facile and the cost of NiO is very low, this NiO/carbon cloth anode could be very promising to be applied for high performance, large scale MFCs.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2014.05.015>.

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